UDC 55 CODEN – GEOME 2 ISSN 0352 – 1206

GEOLOGICA MACEDONICA

Geologica Macedonica	Год. 13	стр. 1–104	Штип 1999
Geologica Macedonica	Vol.	pp.	Štip

GEOME 2
Manuscript received: March 28, 1999
Accepted: November 29, 1999

Geologica Macedonica, Vol. 13, p. 69–74 (1999)
ISSN 0352 – 1206
UDC: 549.1 (497.7)

Original scientific paper

MINERALS FROM MACEDONIA

III. DETERMINATION OF CALCITE AND ARAGONITE IN MINERAL MIXTURES USING FT IR SPECTROSCOPY

Gligor Jovanovski[1], Viktor Stefov[1], Bojan Jovanovski[1], Bojan Šoptrajanov[1], Blažo Boev[2]

[1]*Faculty of Sciences, Institute of Chemistry,*
P.O. Box 162, 91001 Skopje, Republic of Macedonia
e-mail: gligor@robig.pmf.ukim.edu.mk
[2]*Faculty of Mining and Geology, Štip, Republic of Macedonia*
e-mail: b.boev@rudar.mpt.com.mk

A b s t r a c t : The appearance of the ν_1 mode (1083 cm^{-1}) in the FT IR spectrum of aragonite (absent in the spectrum of calcite) as well as the lower frequency of the ν_4 mode in the spectrum of aragonite (713 and 700 cm^{-1}) than in that of calcite (732 cm^{-1}) made it possible to detect the presence of aragonite in calcite and to determine its content. Similarly, the higher frequency of the ν_4 mode in the spectrum of calcite (732 cm^{-1}) than in aragonite (713 and 700 cm^{-1}) was used to detect impurities as well as to determine the content of calcite in aragonite.

Key words: minerals from Macedonia; calcite; aragonite; detection of impurities; FT IR spectroscopy

INTRODUCTION

Since carbonate minerals, especially the polymorphic forms of $CaCO_3$ (calcite and aragonite) may appear in common minerals, it is advantageous to have rapid and simple methods for detecting impurities of these minerals in one another. With that aim in mind and as a part of a broader study of the structural and spectroscopic characteristics of metal minerals originating from Macedonia, we studied the analytical application of the FT IR spectra and the powder X-ray diffraction patterns of the carbonate minerals calcite and aragonite (Jovanovski *et al.* 1999a; 1999b). It should be noted, in this context, that the IR and Raman spectra of calcite and aragonite have been previously studied (Frech *et al.*, 1980; Taylor *et al.* 1995) including the suggested method how to distinguish them using FT IR and FT Raman spectroscopy (Tao *et al.* 1998).

As in other methods, the detection of mineral impurities by IR spectroscopy is based on the appearance of selected analytical bands in the spectral regions where other constituents of the studied system do not exhibit absorption.

As is known (Bragg and Claringbull, 1965), calcite crystallizes in the hexagonal system, while aragonite is orthorhombic. The local symmetry of the CO_3^{2-} ions in the structure of calcite type is D_3 and in aragonite it is C_s. The lower local symmetry of the CO_3^{2-} ions in the latter case causes the appearance (around 1083 cm^{-1}) of the ν_1 mode in its IR spectrum. So, contrary to the IR spectrum of the calcite where three bands due to the ν_2, ν_3 and ν_4 modes appear, four modes (ν_1, ν_2, ν_3 and ν_4) are active in the spectrum of aragonite. It is the appearance of the ν_1 mode (1083 cm^{-1}) in the spectrum of aragonite (absent in the calcite spectrum) which enables to detect the presence of small amounts of aragonite in calcite. On the other hand, the higher frequency of the ν_4 mode in the spectrum of calcite (732 cm^{-1}) than the corresponding mode in the spectrum of aragonite (713 and 700 cm^{-1}) makes it possible to use their infrared spectra for detecting impurities of calcite in aragonite.

EXPERIMENTAL

The calcite mineral was from Zletovo while the aragonite mineral sample was taken from 'Ržanovo ore deposit in Macedonia. They were very carefully picked under a microscope from the ore samples.

The appropriate artificial mixtures of calcite and aragonite were prepared by mixing certain amounts of pure minerals, the total mass of the samples always being 2 mg. The calibration curves used to determine the amount of calcite in the corresponding mixtures with aragonite and vice versa were constructed by variation of the mass fraction of calcite/aragonite from 0 to 0.5.

The infrared spectra of the samples were recorded on a Perkin-Elmer FT IR system 2000 using the KBr pellet method. The acquisition of the spectra was done by using the GRAMS ANALYST 2000 package (GRAMS ANALYST for PE 2000 FTIR, Vers. 3.01 B, Galactic Industries Corporation, 1991–1993) whereas for manipulations on the recorded spectra the GRAMS32 (GRAMS32 for Microsoft Windows, Vers. 4.10, Galactic Industries Corporation, 1991–1996) package was employed.

MINERAL ASSOCIATIONS OF ZLETOVO AND 'RŽANOVO ORE DEPOSITS

Six types of paragenesis exist in the Zletovo ore deposit. Calcite appears in two of them:

– *Medium- to low-temperature sulfide-sulfosalt paragenesis*: (enargite, bornite, chalcopyrite, pyrite, sphalerite, galenite, tetrahedrite, tennantite, luzonite, famatinite, bizmuthian, chalcocite, bournonite, boulangerite, freibergite, proustite, pyrargyrite, siderite, rhodochrosite, **calcite**, barite, quartz);

– *Low-temperature oxide-carbonate paragenesis:* (siderite, rhodochrosite, **calcite**, barite, quartz, chalcedony).

More detailed information about mineral composition and ore parageneses of Zletovo deposit could be found in previously published papers (Cisarc and Rakić, 1956; Radusinović, 1961; Denkovski, 1974; Rakić, 1978; Blečić, 1981; Zarić, 1982; Serafimovski, 1993).

Within the serpentinized ultrabasic rocks of the 'Ržanovo ore deposit, it is often possible to find many veins filled with fibrous white minerals, calcite, dolomite and **aragonite**. Sometimes these veins could be thick up to 80 cm.

More details about geological position and characteristics of the 'Ržanovo ore deposit are given in papers by one of us and by other authors (e.g. Ivanov, 1959; Grafenauer and Strmole, 1960; Maksimović, 1981; Boev, 1982; Boev and Stojanov, 1985; Boev and Lepitkova, 1994).

RESULTS AND DISCUSSION

Aragonite in calcite

The infrared spectra of pure calcite and aragonite are shown in Fig. 1. The spectra of mixtures of calcite with aragonite are presented in Fig. 2. As seen from Fig. 2, the increase of the aragonite content results in an augmentation of the 1083 cm^{-1} band intensity. The relationship between the integral intensity of the analytical band (1090–1075 cm^{-1}) and the mass fraction (w) of aragonite in the aragonite–calcite mixtures is linear (Fig. 3), the regression analysis leading to the equation:

$$\text{integral intensity} = 8.055 \cdot 10^{-3} \cdot w(\text{aragonite}) + 4.488 \cdot 10^{-2}$$

with a correlation coefficient $r = 0.9976$.

The precision of the method was determined as the relative standard deviation of the measured values for the integral intensities of the 1090–1075 cm^{-1} band for each of the prepared standard mixtures from the respective values calculated by regression. It was found that σ_r ranges from 0.67 % to 10.38 % which can be considered as satisfactory precision. By determining the value of the standard deviation σ in the case of the sample with the minimal value for the aragonite mass fraction (2 %), the limit of detection (taken to be equal to 3σ) was found to be 0.833 %.

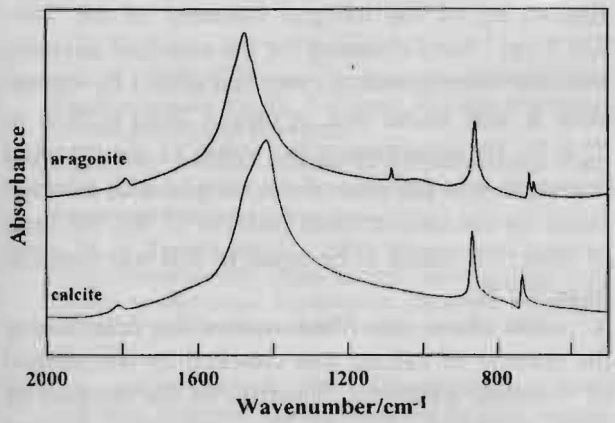

Fig. 1. The FT IR spectra of calcite and aragonite

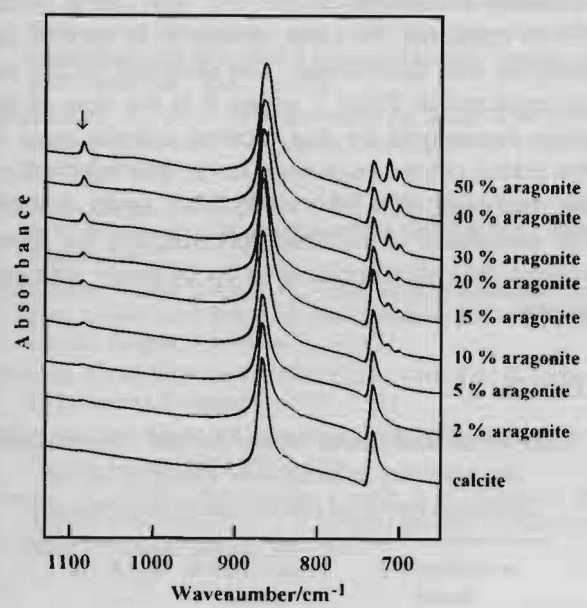

Fig. 2. The FT IR spectra of calcite and mixtures of calcite with aragonite

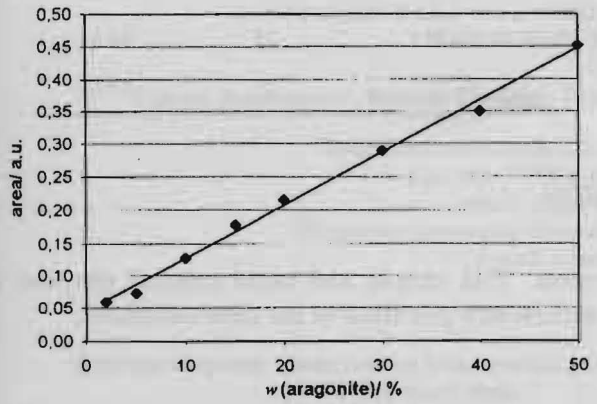

Fig. 3. The relationship between the integral intensity of the analytical band (1090–1075 cm^{-1}) and the mass fraction (w) of aragonite in the aragonite-calcite mixtures

The above described method for determining the content of aragonite was checked by the method of standard additions. Namely, in the samples of pure calcite, varying (but precisely known) amounts of aragonite were added and the infrared spectra were recorded. By substituting the corresponding intensities of the 1090–1075 cm^{-1} band in the above equation, the mass of aragonite in each of the samples was determined. The results thus obtained are summarized in Table 1, where R is the ratio (expressed in %) of the mass determined by this method and the mass of the added aragonite. The high values for R (95.6 – 105.0 %) confirm the usefulness of infrared spectroscopy for determining the aragonite content in its mixtures with calcite.

Table 1

Calculated and found values for the aragonite mass fraction (w) in calcite using infrared spectroscopy and the obtained recovery coefficients

w (aragonite) / % found	w (aragonite) / % added	R / %
3.82	4	95.64
6.76	7	96.52
16.26	17	95.64
25.86	25	103.46
36.77	35	105.05

Calcite in aragonite

The infrared spectra of aragonite samples containing calcite are given in Fig. 4.

The relationship between the relative intensity of the corresponding analytical band (740–724.5 cm^{-1}) and the mass fraction of calcite in the calcite-aragonite mixtures is given in Fig. 5.

As seen from Fig. 4, the augmentation of the calcite content expectedly results in an increase of the 732 cm^{-1} band intensity. The relationship between the relative intensity of the 740–724.5 cm^{-1} analytical band and the mass fraction of calcite in the calcite–aragonite mixtures is linear (Fig. 5), the regression analysis leading to the equation:

$$\text{integral intensity} = 3.044 \cdot 10^{-2} \cdot w(\text{calcite}) - 1.614 \cdot 10^{-2}$$

with a correlation coefficient $r = 0.993$.

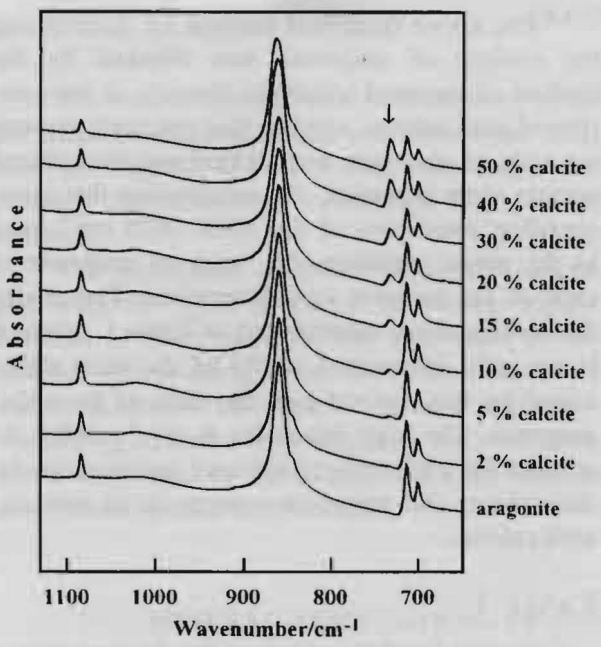

Fig. 4. The FT IR spectra of aragonite and mixtures of aragonite with calcite

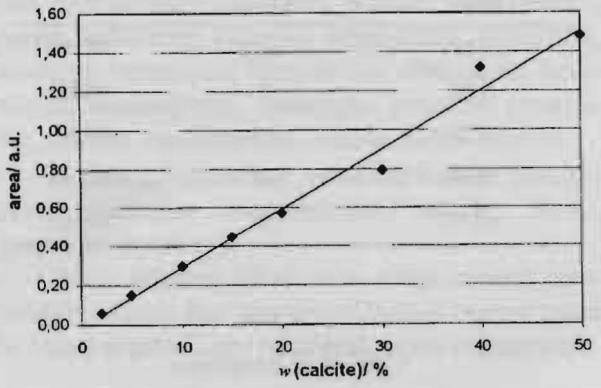

Fig. 5. The relationship between the integral intensity of the analytical band (740–724.5 cm^{-1}) and the mass fraction (w) of calcite in the calcite-aragonite mixtures

As in the previous case, the precision of the method was estimated as the relative standard deviation, σ_r, of the integral intensity of the 740–724.5 cm^{-1} band obtained for the standard mixtures with the corresponding ones calculated by regression. It was found that σ_r ranges from 0.39 % to 22.9 %. By determining the value of the standard deviation σ in the case of the sample with minimal value for the calcite mass fraction (2 %), the limit of detection (taken to be equal to 3σ) was found to be 0.389 %.

The above described method for determining the content of calcite was checked by the method of standard additions. Namely, in the samples of pure aragonite, varying (but precisely known) amounts of calcite were added and the infrared spectra were recorded. By substituting the corresponding intensities of the 732 cm^{-1} band in the above equation, the mass of calcite in each of the samples was determined. The obtained results are summarized in Table 2 where R is the ratio of the mass determined by this method and the mass of the added calcite expressed in %. The high values for recovery (R = 94.6 – 100.2 %) again confirm the usefulness of infrared spectroscopy for determining the calcite content in its mixtures with aragonite.

Table 2

Calculated and found values for the calcite mass fraction (w) in aragonite using infrared spectroscopy and the recovery coefficients

w (calcite) / % found	w (calcite) / % added	R / %
4.01	4	100.19
6.85	7	97.84
16.52	17	97.22
23.70	25	94.81
33.12	35	94.64

CONCLUSION

The present study has shown that the FT IR spectroscopy is a suitable method for determining the content of aragonite in calcite samples and vice versa. This simple and rapid method provides a satisfactory precision of the determinations.

Acknowledgement. The authors are grateful to the authorities of the Zletovo and 'Ržanovo ore deposits in Macedonia for help in collecting of the mineral samples as well as to the Ministry of Science of the Republic of Macedonia for the financial support.

REFERENCES

Блечиќ, Н., 1981: *Студија физичко-хемијских услова ѓенезе лежиста Pb–Zn, Злетово, на бази инклузија рудних раствора*, Београд.

Боев, Б., 1982: *Метаморфизам на руднаша серија 'Ржаново–Студена Вода*. Магистарска теза. Рударско-геолошки факултет, Белград.

Боев, Б., и Лепиткова, С., 1994: *Минерални фази во предредуцираните пелети од металуршкиот процес на Фенимак, Кавадарци*. Зборник на трудови на Рударско-геолошки факултет, Штип, **1**, 231–238.

Boev, B., and Stojanov, R., 1985: *Metamorphism of Ni–Fe pres. from 'Ržanovo–Studena Voda and the Zone Almopias*. Geol. Macedonica, **1**, 191–194.

Bragg, W. L., Claringbull, G. F., 1965: *Crystal Structures of Minerals*, Bell and Sons, London, p. 133.

Cisarc, A., Rakić, S., 1956: *Die Lagerstatten von Zletovo in Macedonien als Beilspiel eins complexen subvulkanisch-hydrothermalen Blei-Zink-Vorkomens*.Vesnik Zavoda za geol. i geof. istr., **XII**, 223–292.

Денковски, Г., 1974: *Минерагенеза на жица 2 во рудникот Добрево*. VIII jugoslovenski geološki kongres, Bled, **5**, 41–54.

Frech, R., Wang, E. C., Bates, J. B., 1980: *The I.R. and Raman Spectra of $CaCO_3$ (aragonite)*. Spectrochim. Acta, **36A**, 915–919.

Grafenauer, S., and Strmole, D., 1960: *Zlog in mineralna sestava nikljenosnih železovih rud 'Ržanova*. Rudarsko-metalurški zbornik, Ljubljana, **1**, 51–62.

GRAMS ANALYST for PE 2000 FTIR, Vers. 3.01 B, Galactic Industries Corporation, 1991–1993.

GRAMS32 for Microsoft Windows, Vers. 4.10, Galactic Industries Corporation, 1991–1996.

Ivanov, T., 1959: *Niklonosno gvožđe kod 'Ržanova na Kožufu (NR Makedonija)*. 3. kongres geologa Jugoslavije, Budva, Zbornik radova, 249–264.

Jovanovski, G., Šoptrajanov, B., Stefov, V., Jovanovski, B., Kaitner, B., 1999: *Some Carbonate Minerals from Macedonia: Analytical Application of their FT IR Spectra and Powder XRD Patterns*. XVI Croatian Meeting of Chemists and Chemical Engineers, Split, Book of Abstracts, E6, 184.

Jovanovski, G., Stefov, V., Jovanovski, B., Šoptrajanov, B., Kaitner, B., 1999: *Minerals from Macedonia: I. Analytical Application of Powder X-ray Diffraction Patterns of Calcite and Aragonite*. XVI Congress of Chemists and Technologists of Macedonia, Skopje, Book of Papers, 43–46.

Maksimović, Z., 1981: *Nickel-bearing phlogopite from the nickel-iron deposit Studena Voda (Macedonia)*. God. Jugosl. cent. kristalogr., **16**, 73.

Radusinović, D., 1961: *Pojave pehblende u Pb–Zn rudniku Zletovo, SR Makedonija*. Radovi Geoinstituta, **1**, 77–84.

Rakić, S., 1978: *Neke strukturne i genetske osobenosti polimetaličnog orudnjenja u Zletovskom rudnom polju*. IX kongres geologa Jugoslavije, Sarajevo, 611–619.

Серафимовски, Т., 1993: *Структурно-металогенетски карактеристики на зоната Леце-Халкидик: Типови на наоѓалишта и рудонасување*. Докторска дисертација, Штип.

Tao, J., Xu, Y., Xu, Z., Wu, J., Xu, D., 1998: *FT-Raman and FT-IR Study on Calcite and Aragonite*. XVIth International Conference on Raman Spectroscopy, Proceedings, Cape Town, 716–717.

Taylor, D. R., Crowther, R. S., Cozart, J. C., Sharrock, P., Wu, J. G., Soloway, R. D., 1995: *Calcium-Carbonate in Cholesterol Gallstones – Polymorphism, Distribution, and Hypotheses about Pathogenesis*. Hepatology, **22**, 488–496.

Зарић, Р., 1982: *Минералошка испитивања у рудniku Zletovo* – studija, Beograd.

Резиме

МИНЕРАЛИ ОД МАКЕДОНИЈА

III. ОПРЕДЕЛУВАЊЕ НА КАЛЦИТ И АРАГОНИТ ВО МИНЕРАЛНИ СМЕСИ СО ПОМОШ НА FT IR СПЕКТРОСКОПИЈА

Глигор Јовановски[1], Виктор Стефов[1], Бојан Јовановски[1], Бојан Шоптрајанов[1], Блажо Боев[2]

[1]*Природно-математички факултет, Институт за хемија, п. фах 162, 91001 Скопје, Република Македонија*
e-mail: gligor@robig.pmf.ukim.edu.mk
[2]*Рударско-геолошки факултет, Штип, Република Македонија*
e-mail: b.boev@rudar.mpt.com.mk

Клучни зборови: минерали од Македонија; калцит; арагонит; определување на нечистотии; FT IR спектроскопија

Појавувањето на модот ν_1 (1083 cm^{-1}) во FT IR спектарот на арагонит (кој е отсутен во спектарот на калцит), како и пониската фреквенција на модот ν_4 во спектарот на арагонит (713 и 700 cm^{-1}) во однос на

соодветната лента во спектарот на калцит (732 cm^{-1}) овозможува да се детектира присуството на арагонит во калцит, но и да се определи неговото количество. Слично, повисоката фреквенција на модот ν_4 во спектарот на калцит (732 cm^{-1}) во споредба со онаа на арагонит (713 и 700 cm^{-1}) е употребена за да се детектира количеството на присутни нечистотии на калцит и арагонит.